FORM PTO 1390 (REV 5-93) US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY DOCKET NUMBER
2001_1159A

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)
09/913736
NEW

International Application No.	International Filing Date	Priority Date Claimed
PCT/JP00/00933	February 18, 2000	February 19, 1999

Title of Invention
METHOD OF REMOVING PHOSPHORIC ACID CONTAINING WASTEWATER

Applicant(s) For DO/EO/US
Takaaki MAEKAWA and Kazuo FUJITA

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.

2. [] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.

3. [X] This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).

4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. [X] A copy of the International Application as filed (35 U.S.C. §371(c)(2))
   a. [] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [X] has been transmitted by the International Bureau.
   c. [] is not required, as the application was filed in the United States Receiving Office (RO/US)

6. [X] A translation of the International Application into English, including Figs. 1-5 (35 U.S.C. §371(c)(2)).

7. [X] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)).
   a. [] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [] have been transmitted by the International Bureau.
   c. [] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [X] have not been made and will not be made.

8. [] A translation of the amendments to the claims under PCT Article 19.

9. [X] An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)). (UNEXECUTED)

10. [] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

Items 11. to 14. below concern other document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. [] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. [X] A FIRST preliminary amendment.

    [] A SECOND or SUBSEQUENT preliminary amendment.

14. [X] Other items or information: (a) Form PCT/IB/308; (b) International Search Report; and (c) First page of published International Application (WO 00/48947).

THE COMMISSIONER IS AUTHORIZED TO CHARGE ANY DEFICIENCY IN THE FEES FOR THIS PAPER TO DEPOSIT ACCOUNT NO. 23-0975

17 AUG 2001

U.S. APPLICATION NO. (If known, see 37 CFR 1.5) NEW 09/913736	INTERNATIONAL APPLICATION NO. PCT/JP00/00933	ATTORNEY'S DOCKET NO. 2001_1159A

15. [X] The following fees are submitted	CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):		
Neither international preliminary examination fee nor international search fee paid to USPTO and International Search Report not prepared by the EPO or JPO $1000.00		
International Search Report has been prepared by the EPO or JPO . . . . . $ 860.00		
International preliminary examination fee not paid ot USPTO but international search paid to USPTO . . . . . $ 710.00		
International preliminary examination fee paid to USPTO but claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . $ 690.00		
International preliminary examination fee paid ot USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . $ 100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$860.00	
Surcharge of $130.00 for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

Claims	Number Filed	Number Extra	Rate		
Total Claims	19 -20 =	0	X $18.00	$	
Independent Claims	3 - 3 =	0	X $80.00	$	
Multiple dependent claim(s) (if applicable)			+ $270.00	$	
TOTAL OF ABOVE CALCULATIONS =				$860.00	
[] Small Entity Status is hereby asserted. Above fees are reduced by 1/2.				$	
SUBTOTAL =				$860.00	
Processing fee of $130.00 for furnishing the English translation later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40 per property +				$	
TOTAL FEES ENCLOSED =				$860.00	
				Amount to be refunded	$
				Amount to be charged	$

a. [X] A check in the amount of $860.00 to cover the above fees is enclosed. A duplicate copy of this form is enclosed.

b. [] Please charge my Deposit Account No. 23-0975 in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0975.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

19. CORRESPONDENCE ADDRESS

000513

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August 17, 2001

[CHECK NO. 46032]

[2001_1159A]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :

Takaaki MAEKAWA et al. : **Attn: BOX PCT**

Serial No. NEW : **Docket No. 2001_1159A**

Filed August 17, 2001 :

METHOD OF REMOVING PHOSPHORIC ACID CONTAINING WASTEWATER
[Corresponding to PCT/JP00/00933 Filed February 18, 2000]

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents,
Washington, DC 20231

Sir:

Please amend the above-identified application as follows:

IN THE SPECIFICATION

Page 1, after the title of the invention, please insert:

This application is a 371 application of PCT/JP00/00933 filed February 18, 2000.

IN THE CLAIMS

Please rewrite the heading "CLAIMES" as follows:

CLAIMS

Please amend claims 3, 4, 6 and 8-10 as follows:

3. (Amended) A method of removing phosphoric acid contained in wastewater as defined in claim 1, wherein the calcium compound is at least one member from calcium hydroxide, inorganic acid salt of calcium and organic carboxylic acid salt of calcium.

4. (Amended) A method of removing phosphoric acid contained in wastewater as defined in claim 1, wherein the polymeric solid is at least one member from polyvinyl alcohol, partially esterified polyvinyl alcohol, polyacrylic acid, partially esterified polyacrylic acid, starch, partially acetylated starch, polysaccharides and partially esterified polysaccharides.

6. (Amended) A method of removing phosphoric acid contained in wastewater as defined in claim 1, wherein the polymeric solid has a multi-layered structure.

8. (Amended) A method as defined in claim 1, wherein the polymeric solid containing calcium or the compound thereof is mechanically vibrated to control surface deposition of calcium phosphate and diffusion of calcium.

9. (Amended) A method as defined in claim 2, wherein the polymeric solid containing calcium or the compound thereof and magnetite is mechanically or electromagnetically vibrated to control surface deposition of calcium phosphate and diffusion of calcium.

10. (Amended) A method as defined in claim 1, wherein formed calcium apatite is recovered in running water.

Please add new claims 13-19 as follows:

13. (New) A method of removing phosphoric acid contained in wastewater as defined in claim 2, wherein the calcium compound is at least one member from calcium hydroxide, inorganic acid salt of calcium and organic carboxylic acid salt of calcium.

14. (New) A method of removing phosphoric acid contained in wastewater as defined in claim 2, wherein the polymeric solid is at least one member from polyvinyl alcohol, partially esterified polyvinyl alcohol, polyacrylic acid, partially esterified polyacrylic acid, starch, partially acetylated

starch, polysaccharides and partially esterified polysaccharides.

15. (New) A method of removing phosphoric acid contained in wastewater as defined in claim 14, wherein the polymeric solid is a gelled polyvinyl alcohol or a partial esterification product thereof.

16. (New) A method of removing phosphoric acid contained in wastewater as defined in claim 2, wherein the polymeric solid has a multi-layered structure.

17. (New) A method of removing phosphoric acid contained in wastewater as defined in claim 16, wherein the polymeric solid is formed with a coating layer of calcium alginate.

18. (New) A method as defined in claim 2, wherein the polymeric solid containing calcium or the compound thereof is mechanically vibrated to control surface deposition of calcium phosphate and diffusion of calcium.

19. (New) A method as defined in claim 2, wherein formed calcium apatite is recovered in running water.

REMARKS

The specification has been amended to insert a cross-reference to the International Application.

The claims have been amended to avoid the improper multiple dependency of some of them, and also to avoid the multiple dependent claim fee.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "**Version with markings to show changes made.**"

As a result of these amendments, new claims 13-19 have been added to the application. These new claims are the same as claims 3-8 and 10, respectively, except for their dependency.

Respectfully submitted,

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August 17, 2001

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Version with Markings to Show Changes Made

CLAIMS

1. A method of removing phosphoric acid contained in wastewater, which comprises inclusively fixing calcium or a compound thereof in a polymeric solid, and bringing the same with wastewater to form calcium apatite by reaction between phosphoric acid in wastewater and calcium.

2. A method of removing phosphoric acid contained in wastewater, which comprises inclusively fixing calcium or a compound thereof and magnetite in a polymeric solid, and bringing the same with wastewater to form calcium apatite by reaction between phosphoric acid in wastewater and calcium.

3. A method of removing phosphoric acid contained in wastewater as defined in claim 1 ~~or 2~~, wherein the calcium compound is at least one member from calcium hydroxide, inorganic acid salt of calcium and organic carboxylic acid salt of calcium.

4. A method of removing phosphoric acid contained in wastewater as defined in ~~any one of~~ claims 1 ~~to~~ 1, wherein the polymeric solid is at least one member from polyvinyl alcohol, partially esterified polyvinyl alcohol, polyacrylic acid, partially esterified polyacrylic acid, starch, partially acetylated starch, polysaccharides and partially esterified polysaccharides.

5. A method of removing phosphoric acid contained in wastewater as defined in claim 4, wherein the polymeric solid is a gelled polyvinyl alcohol or a partial esterification product thereof.

6. A method of removing phosphoric acid contained in wastewater as defined in ~~any one of~~ claim 1 ~~to~~ 5, wherein the polymeric solid has a multi-layered structure.

7. A method of removing phosphoric acid contained in wastewater as defined in claim 6, wherein the polymeric solid is formed with a coating layer of calcium alginate.

8. A method as defined in ~~any one of~~ claims 1 ~~to 7~~, wherein the polymeric solid containing calcium or the compound thereof is mechanically vibrated to control surface deposition of calcium phosphate and diffusion of calcium.

9. A method as defined in ~~any one of~~ claims 2 ~~to 7~~, wherein the polymeric solid containing calcium or the compound thereof and magnetite is mechanically or electromagnetically vibrated to control surface deposition of calcium phosphate and diffusion of calcium.

10. A method as defined in ~~any one of~~ claims 1 ~~to 9~~, wherein formed calcium apatite is recovered in running water.

11. An inclusion immobilizing support for removing phosphoric acid in wastewater wherein calcium or a compound thereof is supported on a polymeric solid.

12. A support as defined in claim 11 wherein the magnetite is contained in the polymeric solid.

METHOD OF REMOVING PHOSPHORIC ACID CONTAINING WASTEWATER

TECHNICAL FIELD

The invention of the present application concerns a method of removing phosphoric acid from general domestic wastewater, industrial wastewater or the like. Further, more in particular, the invention of the present application concerns a method of removing phosphoric acid from domestic wastewater, as well as various kinds of wastewater discharged from food industries and agricultural production fields.

BACKGROUND ART

The concentration of phosphoric acid in domestic wastewater is about 2 to 3 mg/L and removal of phosphoric acid in the domestic wastewater has become an important subject for the requirement of removing phosphoric acid from wastewater, for example, from food industries and agricultural production fields, as well as for preventing eutrophication rivers and lakes.

In view of the subject described above, studies have been made so far on the removal of phosphoric acid. Then, a method of removing phosphoric acid by reacting phosphoric acid in a solution containing calcium in excess has been proposed. However, since this existent method is adapted to add a calcium solution to liquid wastes containing phosphoric acid by way of a pump or the like, it has been a problem that calcium can not easily be added in domestic wastewater draining channels.

DISCLOSURE OF THE INVENTION

In view of the above, for solving the subject in the prior art as described above and facilitating addition of calcium to wastewater, the inventors of the present application have invented a method of gradually releasing calcium by supports including calcium and adding the same to wastewater in draining channels.

That is, the invention provides, at first, a method of removing phosphoric acid contained in wastewater, which comprises including and immobilizing calcium or a compound thereof in a polymeric solid, bringing the same into contact with wastewater and forming calcium apatite by the reaction between phosphoric acid in wastewater and calcium.

Further, the invention provides, secondly, a method of removing phosphoric acid contained in wastewater, which comprises including and immobilizing calcium or a compound thereof and magnetite in a polymeric solid, bringing the same into contact with wastewater and forming calcium apatite by the reaction between phosphoric acid in wastewater and calcium.

The invention provides, thirdly, the method described above in which the calcium compound is at least one member from water solubilized calcium, inorganic acid salt of calcium and organic carboxylic acid salt of calcium, fourthly, the method as described above in which the polymeric solid is at least one member from polyvinyl alcohol, partially esterified polyvinyl alcohol, polyacrylic acid, partially esterified polyacrylic acid, starch, partial acetylated starch, polysaccharides and partial esterified product of polysaccharides, fifthly, the method as described above in which the polymeric solid is a gelled polyvinyl alcohol or a partially

esterified product thereof, sixthly, the method as defined above in which the polymeric solid has a multi-layered structure and, seventhly, the method described above in which the polymeric solid is formed with a coating layer of calcium alginate.

Then, the invention provides, eighthly, a method of controlling surface deposition of calcium phosphate and diffusion of calcium by mechanically vibrating a polymeric solid containing calcium or a compound thereof, ninthly, a method of controlling surface deposition of calcium phosphate and diffusion of calcium by mechanically or electromagnetically vibrating a polymeric solid containing calcium or a compound thereof and magnetite, and, tenthly, a method of recovering calcium apatite formed in running water.

Further, the invention provides, eleventhly, an inclusive immobilizing support for removing phosphoric acid in wastewater in which calcium or a compound thereof is supported on a polymeric solid, and, twelfthly, an inclusion immobilizing support in which magnetite is contained in the polymeric solid.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a cross sectional view illustrating an example of a mechanical vibration system.

Fig. 2 shows a cross sectional view illustrating an example of a vibration system using an electromagnet.

Fig. 3 shows an outlined constitutional view illustrating an example of a processing system in which a settling tank is disposed.

Fig. 4 shows a graph illustrating the result of processing in a case where seed crystals are not present.

Fig. 5 shows a graph illustrating the result of processing

in a case where seed crystals are present.

References in the drawings, denote the followings.

(1) immobilizing support

(2) net

(3) processing tank

(4) magnet

(5) drain channel

(6) settling tank

(7) calcium apatite crystal

(8) cage

BEST MODE FOR CARRYING OUT THE INVENTION

The invention has the features as described above and the mode of practicing thereof is to be explained.

In the invention, an inclusion solid support in which calcium is supported on a polymeric solid is used for removing phosphoric acid in wastewater. The polymeric solid in this case, more preferably contains magnetite, and various kinds of materials may be used so long as they have satisfactory supporting property for calcium and, for example, polymers having anionic groups such as hydroxy groups or carboxyl groups, and like other various kinds of materials may be used. For example, more preferred materials may include polyvinyl alcohol (PVA), partially esterification (such as acetylation) products thereof, polyacrylic acid, partial esterification products (methyl esters), starch powder, partial acetylation products thereof, as well as other polysaccharides.

Calcium may be supported on the polymeric solid as calcium or as a calcium compound such as calcium hydroxide, calcium carbonate, calcium chloride and calcium organic carboxylate.

For the support to the polymeric solid in the invention of the present application, it may have a multi-layered structure. For example, calcium hydroxide or calcium carbonate may be kneaded into acetylated starch, which is molded into a spherical or pellet shape and then a PVA layer may be formed to the surface of the molding product by using an aqueous solution of polyvinyl alcohol (PVA). Further, it may consist only of PVA without using starch.

Then, since water-containing PVA has a strong solid structure by repetitive refrigeration and thawing into a gel, the repetitive processing of refrigeration and thawing is effective.

The refrigeration in this case is preferably conducted as a processing within a range from -30°C to -15°C for 20 to 60 hours.

Further, it is preferred that the PVA concentration of the aqueous solution of PVA is from 5 to 20% by weight, the average molecular weight of PVA is from 1000 to 4000 and, more preferably, 1500 to 2500. Further, the degree of gelation is preferably 80% or more,

For the size of the polymeric solid, the maximum outer diameter, for example, is suitably from 3 to 20 mm.

In the invention of the present application, by utilizing the nature of alginic acid ions of chemically bonding with calcium ions to form a polymer, alginic acid may be coated on the surface of the polymeric solid described above, which is then treated with a solution such as of calcium chloride, to form a layer of calcium alginate.

The concentration of alginic acid in this case is suitably from 0.2 to 1.0% by weight.

It is of course possible to form a PVA coating layer further on the coating of calcium alginate as described above and gelling the same by repetitive refrigeration and thawing. Although not always necessary, magnetite is incorporated into the polymer for providing the polymer with magnetic property and make the support displaceable or movable by magnetic fields generated by magnetic field forming means (for example, electromagnet or permanent magnet disposed) to a wastewater processing tank or to the outside of a wastewater processing zone. The magnetite may be a powder of super-paramagnetic material not adhering to each other if the magnetic field is not present. For instance, it may be a powder of oxide of metals such as iron.

The method of the invention and the immobilizing support used therefor can include an embodiment that supported calcium reacts with phosphoric acid in wastewater on the surface of the immobilizing support or in a state released in the solution to form calcium phosphate, that is, calcium apatite, which may be separated as recovered as crystals.

In a state where calcium phosphate crystals are deposited as they are on the surface of the support, since diffusion of calcium may possibly be hindered, deposition of crystals on the surface of the support can be prevented, for example, as shown in Fig. 1, by enclosing an immobilizing support (1) with a net (2) of a large pore size or the like, which is placed in a processing tank (3) and vibrated mechanically. Further, deposition of crystals to the surface of the support can be prevented in the same manner also by incorporating magnetite to the support (1) of the polymeric solid and vibrating them by changing the magnetic fields by an electromagnet (4) disposed at the periphery as shown in Fig.2.

Also with the view point of controlling the releasing density of calcium, the releasing rate can be controlled by vibrating the support by the methods described above.

While obtained calcium apatite crystals can be re-used, for example, as fertilizers, it is desired that they are recovered by a more simple method so as not to be discharged from the draining channel. Various kinds of means may be considered for this purpose. For example, as shown in Fig. 3, calcium apatite crystals (7) can be separated and recovered easily from wastewater by disposing a setting tank (6) at the terminal end of the draining channel (5) and periodically recovering them. Releasing or diffusion of calcium from the immobilizing support can be controlled, for example, in accordance with concentration of PVA or the like as the polymer of the immobilizing support, calcium concentration, thickness of the immobilizing support and vibration speed. It is essential to prevent inhibition of calcium diffusion in a case where reaction is taken place on the surface of the support. Calcium phosphate can be re-used as a fertilizer by periodical recovering operation by diffusing calcium in the inside of the support by compulsory vibration, accumulating calcium apatite as reaction products to the settling tank and recovering them periodically. In this case, the calcium containing polymeric support is exchanged, for example, periodically.

In the embodiment shown in Fig. 3, the calcium containing polymeric support (1) is placed, for example, in an easily vibrated cage (8) and dipped in a place of a draining channel (5) where wastewater runs and the cage (8) or the like is disposed at the succeeding place so that the cage (8) can be vibrated mechanically or electrically, but it is not restricted only

to such an example. The processing conditions are set appropriately and the immobilizing support may be of a fixed bed or a fluidized bed.

Then, examples are shown next and the invention is to be explained more in details.

EXAMPLE

Example 1

Method of preparing calcium-containing immobilizing support

<A> For the support of calcium, calcium hydroxide or quick lime is kneaded with acetylated starch at 1 : 1 (weight ratio) and prepared into a 5 - 10 mm spherical or pellet shape by an extrusion molding machine, which is dropped into an aqueous 10 to 15 wt% solution of PVA, on which a thin layer is formed.

It is preferred that the average molecular weight of PVA is about 2000 and the saponification degree thereof is about 95% or more. An aqueous solution of PVA at 10 to 15% by weight is prepared and used. Since water-containing PVA molecules have a nature of releasing water molecules from the solid structure of the polymer to be gelled and form a strong structure when repeating refrigeration and thawing, this property is utilized. Specifically, it was frozen at a low temperature of about -20°C for 24 to 48 hours, which is repeated for 2 - 3 times to progress polymerization of PVA and enhance the physical strength. The substitution degree of acetylation for the acetylated starch and the size of the porous gel of the PVA polymer obtained by the operation control the releasing speed of the calcium ions.

<B> Further, since alginic acid ions have a property of chemically bonding with calcium ions to form a polymer and become

insolubilized, this property can be utilized for the coating of the surface of the polymeric solid. Specifically, the polymeric solid is dropped in an aqueous solution of alginic acid at 0.5 to 5% by weight, or an aqueous solution of alginic acid at 0.5 - 5% by weight is sprayed on the surface of the polymeric solid, which is dropped in a saturated solution of calcium chloride. Then, the thus formed calcium alginate is rendered water insoluble and the coating layer is formed thereon with the aqueous solution of PVA at 10 to 15 wt% described above, and refrigeration is repeated for 2 to 3 times at a low temperature of about -20°C to gel the same.

<C> When the magnetite is used, 1.5 to 3.0 g of magnetite is previously mixed preferably to 50 - 100 ml of an aqueous solution of PVA before polymerization by refrigeration or the like, which is then used.

Example 2

Calcium is supported to form an inclusion immobilizing support as in Example 1<A>. A solution at an initial phosphoric acid concentration of 3 mg/L was processed by using the same. Fig. 4 shows a relation between the processing time and the change of the phosphoric acid solution in a case of not adding calcium chloride as seed crystals and Fig. 5 shows that in a case of adding the seed crystals.

As a result, it was confirmed that the concentration of phosphoric acid can be lowered to about 0.1 to 1 mg/L. Since the phosphoric acid concentration in domestic wastewater draining channel is usually about several mg/L, it can be expected for a removing ratio of about 80% to 90%. It is considered that the final concentration is about 0.5 mg/L also in a case where the concentration of phosphoric acid is higher than several

mg/L.

According to the invention of the present application, excellent effects can be obtained in that (1) calcium can be added easily by including and immobilizing calcium in the polymer, (2) surface deposition and diffusion of calcium can be controlled by vibrating the magnetite-containing polymer electrically or mechanically and (3) calcium apatite crystals can be separated and recovered from wastewater by periodically recovering then in a settling tank disposed at the final end of the draining channel and calcium phosphate can be used again easily as the calcium phosphate in the crystallizing operation of selectively removing phosphoric acid in wastewater in the draining channels.

CLAIMES

1. A method of removing phosphoric acid contained in wastewater, which comprises inclusively fixing calcium or a compound thereof in a polymeric solid, and bringing the same with wastewater to form calcium apatite by reaction between phosphoric acid in wastewater and calcium.

2. A method of removing phosphoric acid contained in wastewater, which comprises inclusively fixing calcium or a compound thereof and magnetite in a polymeric solid, and bringing the same with wastewater to form calcium apatite by reaction between phosphoric acid in wastewater and calcium.

3. A method of removing phosphoric acid contained in wastewater as defined in claim 1 or 2, wherein the calcium compound is at least one member from calcium hydroxide, inorganic acid salt of calcium and organic carboxylic acid salt of calcium.

4. A method of removing phosphoric acid contained in wastewater as defined in any one of claims 1 to 3, wherein the polymeric solid is at least one member from polyvinyl alcohol, partially esterified polyvinyl alcohol, polyacrylic acid, partially esterified polyacrylic acid, starch, partially acetylated starch, polysaccharides and partially esterified polysaccharides.

5. A method of removing phosphoric acid contained in wastewater as defined in claim 4, wherein the polymeric solid is a gelled polyvinyl alcohol or a partial esterification product thereof.

6. A method of removing phosphoric acid contained in wastewater as defined in any one of claim 1 to 5, wherein the polymeric solid has a multi-layered structure.

7. A method of removing phosphoric acid contained in wastewater as defined in claim 6, wherein the polymeric solid is formed with a coating layer of calcium alginate.

8. A method as defined in any one of claims 1 to 7, wherein the polymeric solid containing calcium or the compound thereof is mechanically vibrated to control surface deposition of calcium phosphate and diffusion of calcium.

9. A method as defined in any one of claims 2 to 7, wherein the polymeric solid containing calcium or the compound thereof and magnetite is mechanically or electromagnetically vibrated to control surface deposition of calcium phosphate and diffusion of calcium.

10. A method as defined in any one of claims 1 to 9, wherein formed calcium apatite is recovered in running water.

11. An inclusion immobilizing support for removing phosphoric acid in wastewater wherein calcium or a compound thereof is supported on a polymeric solid.

12. A support as defined in claim 11 wherein the magnetite is contained in the polymeric solid.

Fig.1

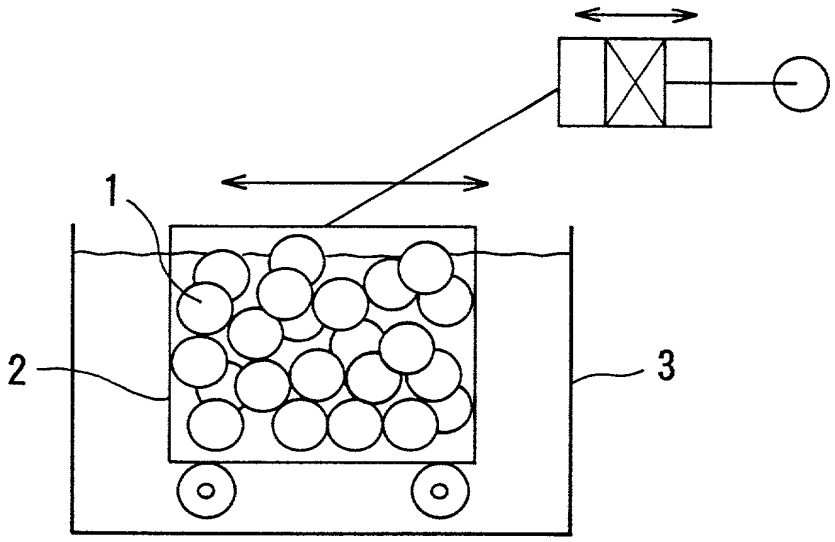


Fig.2

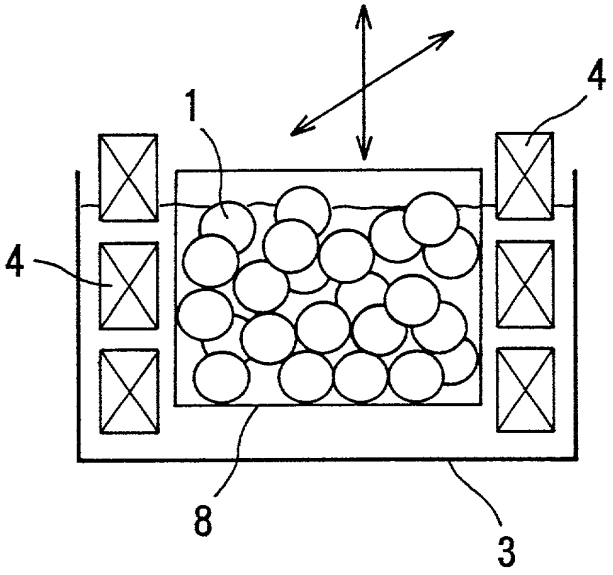


Fig.3

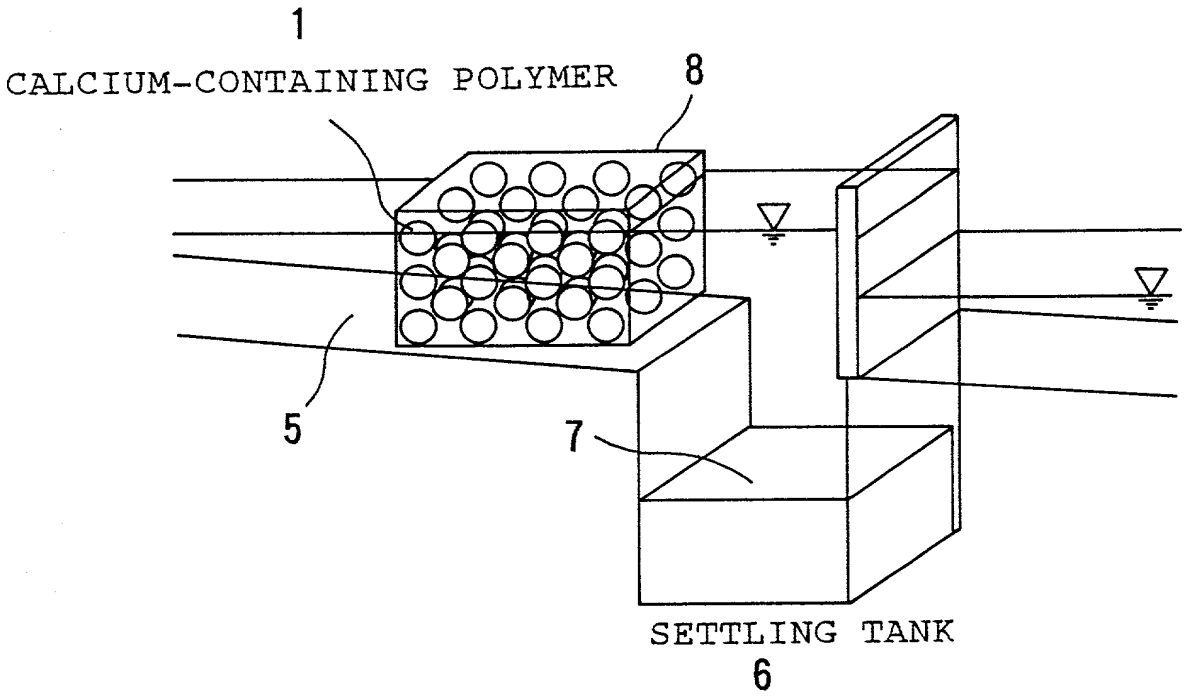


Fig.4

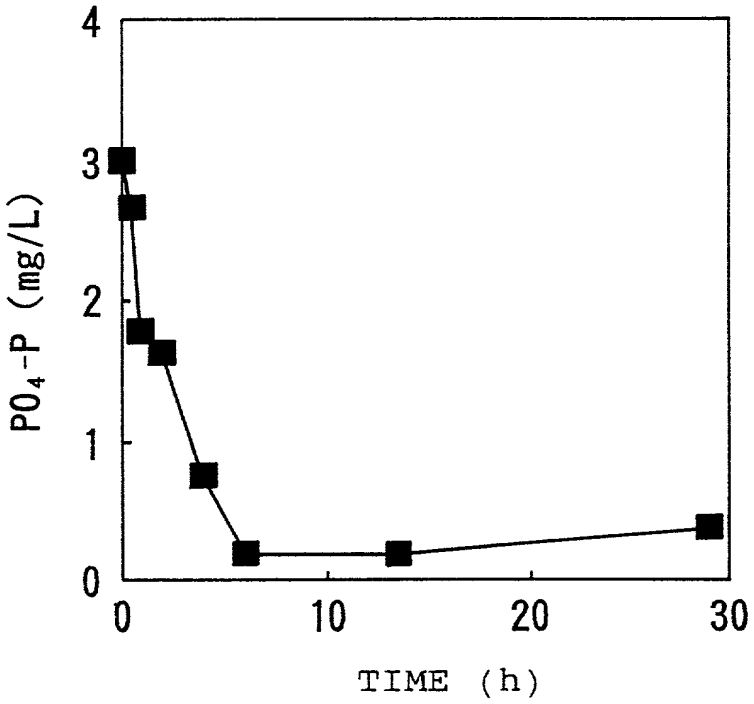
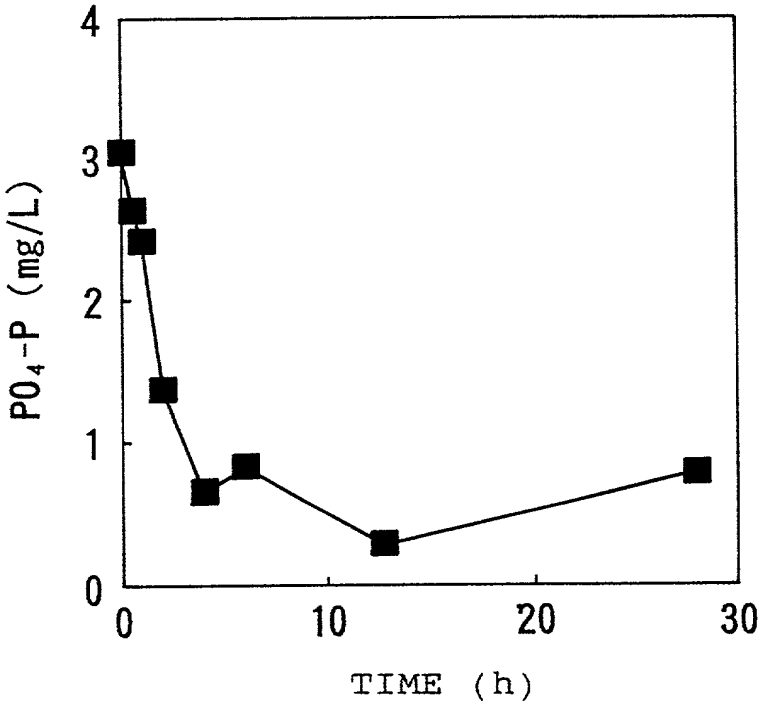


Fig.5



Rev. 3-21-01 Effective March 1998

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION

(X) Original () Supplemental () Substitute () PCT () DESIGN

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Title: METHOD OF REMOVING PHOSPHORIC ACID CONTAINING WASTEWATER

of which is described and claimed in:
() the attached specification, or
() the specification in application Serial No., filed , and with amendments through _____, or
(X) the specification in International Application No. PCT/JP00/00933, filed February 18, 2000, and as amended on _(if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any application(s) for patent or inventor's certificate listed below and have also identified below any application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
Japan	**1999-041970**	**February 19, 1999**	**yes**

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

And I hereby appoint Michael R. Davis, Reg. No. 25,134; Matthew M. Jacob, Reg. No. 25,154; Warren M. Cheek, Jr., Reg. No. 33,367; Nils Pedersen, Reg. No. 33,145; Charles R. Watts, Reg. No. 33,142; and Michael S. Huppert, Reg. No. 40,268, who together constitute the firm of WENDEROTH, LIND & PONACK, L.L.P., as well as any other attorneys and agents associated with Customer No. 000513, to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys and agents named herein to accept and follow instructions from NISHIZAWA & ASSOCIATES as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

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I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor Takaaki Maekawa Takaaki MAEKAWA Date September 19, 2001

2nd Inventor Kazuo Fujita Kazuo FUJITA Date September 19, 2001

3rd Inventor _____ Date _____

4th Inventor _____ Date _____

5th Inventor _____ Date _____

6th Inventor _____ Date _____

The above application may be more particularly identified as follows:

U.S. Application Serial No. 09/913,736 Filing Date August 17, 2001

Applicant Reference Number 99-F-049PCT-US/NT Atty Docket No. 2001_1159A

Title of Invention METHOD OF REMOVING PHOSPHORIC ACID CONTAINING WASTEWATER